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THE DECOMPOSITION OF DIETHYL PEROXIDE IN THE PRESENCE OF NITRIC OXIDE AND ETHYL NITRITE

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ABSTRACT: The reaction of ethoxyl radicals with ethyl nitrite, nitric oxide and a mixture of these, all in the vapor phase, has been studied. The radicals were produced by the decomposition of diethyl peroxide at 181°C.

The impact of the results of these studies on the mechanisms for the thermal decomposition of both nitrate and nitrite esters is discussed and revised mechanisms suggested.

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The research reported herein was done under task assignment NOL-Re2d-02-1-53. The results obtained here are of importance for the mechanisms of decomposition of nitrite and nitrate esters and indicate certain necessary revisions in these mechanisms and in turn in the mechanism of thermal decomposition of nitrate ester propellants.

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THE DECOMPOSITION OF DIETHYL PEROXIDE IN THE PRESENCE OF NITRIC OXIDE AND ETHYL NITRITE

INTRODUCTION

Recent studies in this laboratory have revealed that in the thermal decomposition of ethyl nitrate, a major product is ethyl nitrite (a). It seems quite likely that such products are typical for nitrate esters and an understanding of how they arise is basic to an understanding of how nitrate esters decompose. In a previous report (a) two possible routes to nitrite ester formation were discussed. One route was the reaction of nitrogen dioxide and alcohols:

$$C_2H_5OH + 2NO_2 \longrightarrow C_2H_5ONO + HONO_2 \qquad (1)$$

It was pointed out that this route was inadequate to explain the amount of nitrite ester formed.

The other route discussed involved the reaction of alkoxyl radicals with nitric oxide:

$$C_2H_5O\cdot + NO \longrightarrow C_2H_5ONO \qquad (2)$$

Evidence on the feasibility of this route was found in studies on the thermal decomposition of nitrite esters. This reaction which is quite similar to the thermal decomposition of nitrate esters has been thoroughly studied (b) and the following mechanism is currently accepted:

$$C_2H_5ONO \longrightarrow C_2H_5O\cdot + NO \qquad (3)$$

$$C_2H_5O\cdot + C_2H_5ONO \longrightarrow C_2H_5OH + CH_3\overset{H}{\underset{\cdot}{C}}ONO \qquad (4)$$

$$CH_3\overset{H}{\underset{\cdot}{C}}ONO \longrightarrow CH_3CHO + NO \qquad (5)$$

Comparison of this with the mechanism suggested for nitrate esters (c) shows that they are analogous and any evidence gained about the mechanism of nitrite ester decomposition would have direct bearing on the mechanism of nitrate ester decomposition.

The decomposition of all the nitrite esters studied (b) follow first order kinetics. This requires that the reverse of the initial step, i.e. reaction (2) must be very slow compared with the second step, reaction (4). It seemed that if this were so then the same thing would be true for nitrate esters and reaction (2) as a route to the nitrite esters would be invalid.

It is somewhat puzzling to consider that reaction (2) should be slow compared to (4). Reaction (2) is a reaction between two free radicals and probably has an activation energy that is zero, or very low (d). It would be expected to be a very fast reaction.

It therefore seemed desirable to investigate this point further. It has been possible to compare the relative velocities of reactions (2) and (4) directly and the results of this investigation are the basis of this report.

The Basis of the Experimental Method

The decomposition of diethyl peroxide has recently been studied by Harris and Egerton (e) in a static system over a pressure range of 2 to 30 cm. and by Rebbert and Laidler (f) at very low pressures, using a flow system wherein the peroxide was carried along in a large excess of toluene vapor. The evidence indicates that the first step in the diethyl peroxide decomposition is

$$C_2H_5OOC_2H_5 \rightarrow 2C_2H_5O\cdot \qquad (6)$$

At 181°C the half life of diethyl peroxide as calculated from the data of Harris and Egerton (e) is about 8 seconds while that for ethyl nitrite is about 130 minutes (g). By heating a mixture of diethyl peroxide, nitric oxide and ethyl nitrite at 181°C for a few minutes it should be possible in essence to generate ethoxyl radicals in the presence of ethyl nitrite and nitric oxide and by measuring the change in ethyl nitrite pressure to get a measure of the comparative velocities of reactions (2) and (4).

Experimental Part

Chemicals

The ethyl nitrite used was prepared in standard fashion (g), distilled and a middle fraction taken. It was stored in sealed ampules in a refrigerator.

The nitric oxide used was purchased from the Matheson Company and was certified as 98% pure. It was used directly from the cylinder but further purification was effected by allowing the tube on the bulb filling apparatus containing the nitric oxide to warm up only enough to generate a sufficient pressure of nitric oxide. In this way the higher nitrogen oxides which are the chief impurity were retained in the tube. When a glass photometric cell was filled this way and analyzed for nitrogen dioxide at 4050 Å it was found to be completely transparent.

The diethyl peroxide used was prepared as described by Harris and Egerton (e). The final distillation at atmospheric pressure yielded a product boiling at 62.5 - 63.5°C. The mass spectrographic pattern is shown in Table 1.

Table 1

The Mass Spectrographic Pattern for Diethyl Peroxide

m/e	Intensity	m/e	Intensity	m/e	Intensity	m/e	Intensity
90	16	46	2.32	31	27	19	4.73
74	1.91	45	33	30	5.3	15	17.7
62	30.6	44	4.73	29	100.0	14	2.77
61	2.02	43	14	28	18.7		
59	3.56	42	1.79	27	15.8		
47	3.04	41	2.05	26	3.3		

This pattern is quite similar to that reported by Rebbert and Laidler (f). Here, too, the 29 peak is the strongest and the parent peak is at 90. The presence of a small peak at 74 shows that ethyl ether is present but it is difficult to assess the amount. At any rate, the purity was considered sufficient for the experiments in prospect.

The Analytical Technique

In Figure 1, the infrared spectrum of pure ethyl nitrite taken on a Perkin-Elmer Model 21 Double Beam Infrared Spectrometer is compared to the spectrum of the products obtained when diethyl peroxide is heated with nitric oxide at 181°C. It is clear that ethyl nitrite is the product of this reaction. The peak centering at 12.85μ was that used for the analysis of ethyl nitrite. Diethyl peroxide, its decomposition products, and nitric oxide were found to be transparent in this region. The analysis then simply involved measuring the optical density of the decomposition mixtures at this point and dividing it by the Beer's law constant for ethyl nitrite.

The Beer's law constant for ethyl nitrite at 12.85μ for a pressure of 1 mm. and a cell length of 1 mm. is 0.000847 $\pm$ 0.00002. (a).

The Experimental Measurements

The experiments were carried out by immersing bulbs filled with the appropriate gases in a constant temperature bath for the appropriate time. The reaction was stopped by immersing the bulbs in cold water and the contents were transferred to an infrared cell. This technique is described completely in a previous report (a). It may be noted that in preparing gas mixtures containing ethyl nitrite the ethyl nitrite pressure was measured optically. At the same time that the ethyl nitrite was admitted to a reaction bulb it was admitted to an infrared cell. The pressure was then measured by taking the optical density of the gas in the cell at 12.85μ. This gave a more accurate pressure measurement since the Beer's law constant is calculated on the basis of a large number of pressure measurements and hence is more accurate than a direct pressure reading on the manometer would be.

Results

The experimental results are summarized in Table 2.

Table 2

Products of the Decomposition of Diethyl Peroxide (DEP) in the Presence of Ethyl Nitrite and Nitric Oxide at 181°C

Expt.	Initial Pressure[1] (mm.) DEP	NO	C_2H_5ONO	Time (min.)	Final Pressure[1] of C_2H_5ONO	C_2H_5ONO Produced	Fractional Yield[2] of C_2H_5ONO
1	11.0	22.0	---	1.0	3.7	3.7	0.17
2	10.0	42.0	---	1.0	5.5	5.5	0.28
3	10.0	75.0	---	1.0	3.9	3.9	0.19
4	11.0	22.0	---	2.0	3.7	3.7	0.17
5	11.0	23.0	---	4.0	13.4	13.4	0.61
6	13.8	23.5	---	4.3	16.0	16.0	0.58
7	12.0	22.0	---	6.0	14.1	14.1	0.59
8	11.5	44.0	---	6.0	15.1	15.1	0.66
9	11.0	22.0	10.5	4.0	22.8	12.3	0.56
10	11.0	22.0	---	4.0	12.2	12.2	0.56
11	12.8	---	20.0	4.0	20.2	0.2	---
12	14.0	---	20.0	4.0	20.9	0.9	---

[1] Measured at 25°C

[2] Based on a theoretical yield of 2 moles of ethyl nitrite per mole of diethyl peroxide.

Harris and Egerton (e) have reported a slight induction period for the decomposition of diethyl peroxide. This period is lengthened by the addition of nitric oxide. Thus 30% nitric oxide increased it from 6 seconds to about 2 minutes at 170°C. The low yield in expts. 1-4 is attributed to incomplete decomposition of the diethyl peroxide due to this effect. The lowered yield in expt. 3 as compared to expt. 2 is attributed to the greater inhibition in expt. 3 due to the greater amount of nitric oxide. Judging from expts. 4, 5, 6 and 7 a period of four minutes heating was sufficient to give the maximum yield for the given pressures.

Experiments 9 and 10 are a direct measure of the relative reactivity of nitric oxide and ethyl nitrite with the ethoxyl radical. In expt. 10 as much ethoxyl reacted with nitric oxide in the presence of an amount of ethyl nitrite equal to the nitric oxide as did in expt. 9 where no ethyl nitrite was present. This indicates that the ethoxyl - nitric oxide reaction is much more rapid than the ethoxyl - ethyl nitrite reaction at this temperature. Experiments 11 and 12 are even more decisive. On the basis of two moles of ethoxyl radical per mole of diethyl peroxide more than enough diethyl peroxide was present to decompose all the ethyl nitrite in each experiment. Instead no decomposition occurred. The slight increases observed may be attributed in part to the analytical error and in part to the possible formation of ethyl nitrite from small amounts of nitric oxide present in the ethyl nitrite.

It is not clear what happens to the ethoxyl radicals in expts. 11 and 12. An examination of the infrared spectrum of the products from expt. 11 shows only minor absorption at the acetaldehyde carbonyl absorption at 5.65μ. Due to the tendency of formaldehyde to polymerize to paraformaldehyde its vapor pressure is too low to allow any conclusions to be reached on its presence by means of the infrared spectrum.

It is somewhat puzzling that the maximum yield of ethyl nitrite was only about 0.66. If this were due to a competition between (4) and some other reaction of the ethoxyl radical it would seem that doubling the nitric oxide pressure, expts. 6 and 7, would increase the yield more than it did. It is possible alternatively that this is in part due to an impurity in the diethyl peroxide. The mass spectrograph pattern indicated the presence of ethyl ether, although the amount is uncertain. When a sample of diethyl peroxide was heated by itself to complete decomposition a pressure increase of 104% was obtained. Harris and Egerton (e) report a pressure increase of about 117% for their samples so that it would seem that by this test the material used here was of comparable purity. Since in any case a substantial yield of ethyl nitrite could be obtained it was possible to test the point at issue and this aspect of the experimental work was not pursued further.

The Mechanism of the Decomposition of Alkyl Nitrites

In considering a mechanism for this reaction, the following observations made by Steacie may be considered. Nitric oxide was a major product. On the basis of one nitric oxide molecule per molecule of nitrite decomposed, the yields were about 90%. In addition varying small amounts, 1 - 10%, of carbon monoxide were present as well as small amounts of inert gases. The analyses used by Steacie and Shaw (g) to establish the presence of alcohols and aldehydes as the products were not quantitative but it is quite certain that these products were present in more than trace amount. (Kornblum and Oliveto (h) have recently reported the formation of 2-octanol in 80% yield in the pyrolysis of liquid 2-octyl nitrite.)

It is doubtful whether any arguments can be based on the pressure increases observed during the reaction. These varied from 60% for n-butyl nitrite to 100% for n-propyl nitrite. The final pressures were not constant in any case. The presence of tarry materials in the case of n-propyl and n-butyl nitrites is another complicating factor.

It seems quite likely that the first step in the reaction is (3). The steps suggested by Rice and Rodowskas to give the alcohol and aldehyde must, in the light of the results of Table 2 be incorrect. The only plausible route left for these is

$$C_2H_5O\cdot + C_2H_5O\cdot \longrightarrow C_2H_5OH + CH_3CHO \quad (7)$$

Steps like (7) have been proposed before for alkoxyl radicals (i,j) but (4) has been preferred to (7) because of the much higher concentration of the alkyl nitrite as compared to the alkoxyl radical. This factor is apparently offset by the much lower activation energy of (7). Step (7) is probably accompanied by the reaction suggested by Rice and Rodowskas

$$C_2H_5O\cdot \longrightarrow CH_3\cdot + CH_2O \quad (8)$$

Since (7) is bimolecular and (8) is unmolecular, it will be seen that lower pressures will favor (8) and the yield of ethyl alcohol and acetaldehyde as compared to formaldehyde would depend on the pressure and temperature. Since as mentioned earlier the infrared spectrum of the products in expt. 11 indicates that little acetaldehyde was formed, it appears that at these pressures and at this temperature, (8) predominates over (7). In the other extreme, the pyrolysis of 2-octyl nitrite in the liquid phase, the high yield of alcohol and ketone is consistent with the relatively high concentration of alkoxyl radicals.

Rice and Rodowskas have written as a further reaction of the methyl radical

$$CH_3\cdot + CH_3CH_2ONO \longrightarrow CH_4 + CH_3\overset{H}{C}ONO \quad (9)$$

Since in expt. 11 and 12 there was no induced decomposition of the ethyl nitrite, it appears that here the true fate of the methyl radicals is

$$2CH_3\cdot \longrightarrow C_2H_6 \quad (10)$$

This result is similar to one found by Rebbert and Laidler in the diethyl peroxide decomposition. Despite the presence of a large excess of toluene the major product was ethane and only small amounts of methane and dibenzyl, products of

$$CH_3\cdot + C_6H_5CH_3 \longrightarrow CH_4 + C_6H_5CH_2\cdot$$

$$2C_6H_5CH_2\cdot \longrightarrow C_6H_5CH_2CH_2C_6H_5$$

were found.

The presence of carbon monoxide in the products can be explained here, as it was in the case of diethyl peroxide, (e,f) on the basis of a radical-induced decomposition of the aldehydes.

It thus appears that a satisfactory picture of the alkyl nitrite decomposition is represented by equations (3) (7) (8) and (10) with the sequence (3) (7) predominating at higher pressures and (3) (8) (10) taking over at lower pressures.

Effect of Results on Mechanism of Ethyl Nitrate Decomposition

It is now clear that (2) is a perfectly reasonable route to nitrite ester formation in nitrate ester decomposition. It may be incorporated into a reaction mechanism and the following sequence of equations is one possible scheme:

$$C_2H_5ONO_2 \longrightarrow C_2H_5O\cdot + NO_2$$

$$C_2H_5O\cdot + NO_2 \longrightarrow C_2H_5ONO_2$$

$$C_2H_5O\cdot + NO \longrightarrow C_2H_5ONO$$

$$C_2H_5O\cdot \longrightarrow CH_3\cdot + CH_2O$$

$$CH_3\cdot + NO_2 \longrightarrow CH_3NO_2$$

$$CH_3\cdot + NO_2 \longrightarrow CH_3ONO$$

$$NO_2 + CH_2O \longrightarrow NO + CO + CO_2 + H_2O$$

All of the products found in the ethyl nitrate decomposition are accounted for by the above sequence. There are some serious defects in it. The amounts of ethyl nitrite found in the ethyl nitrate decomposition require that almost one nitrite is formed per nitrate molecule decomposing. The above scheme does not furnish enough nitric oxide to meet this requirement. Furthermore nitromethane and methyl nitrite were found only in small amounts and at the end of the reaction. The above mechanism implies that they would be formed throughout the course of the reaction and in appreciable amount.

The above mechanism does account for the products found better than the previous one (c) and despite the defects pointed out above it can serve as a basis for discussion and as a stimulant to ideas for research in the future.

Summary

The reaction between ethoxyl radicals and nitric oxide at 181°C has been studied using the decomposition of diethyl peroxide as the source of ethoxyl radicals. It has been found that ethyl nitrite is formed. The rate of reaction of ethoxyl radicals with nitric oxide at 181°C has been found to be much greater than that with ethyl nitrite. Decomposition of diethyl peroxide in the presence of ethyl nitrite in fact shows no evidence of reaction involving the nitrite ester.

The implications of these results for the mechanisms of the thermal decomposition of nitrite and nitrate esters are discussed and revised mechanisms suggested.

Acknowledgment

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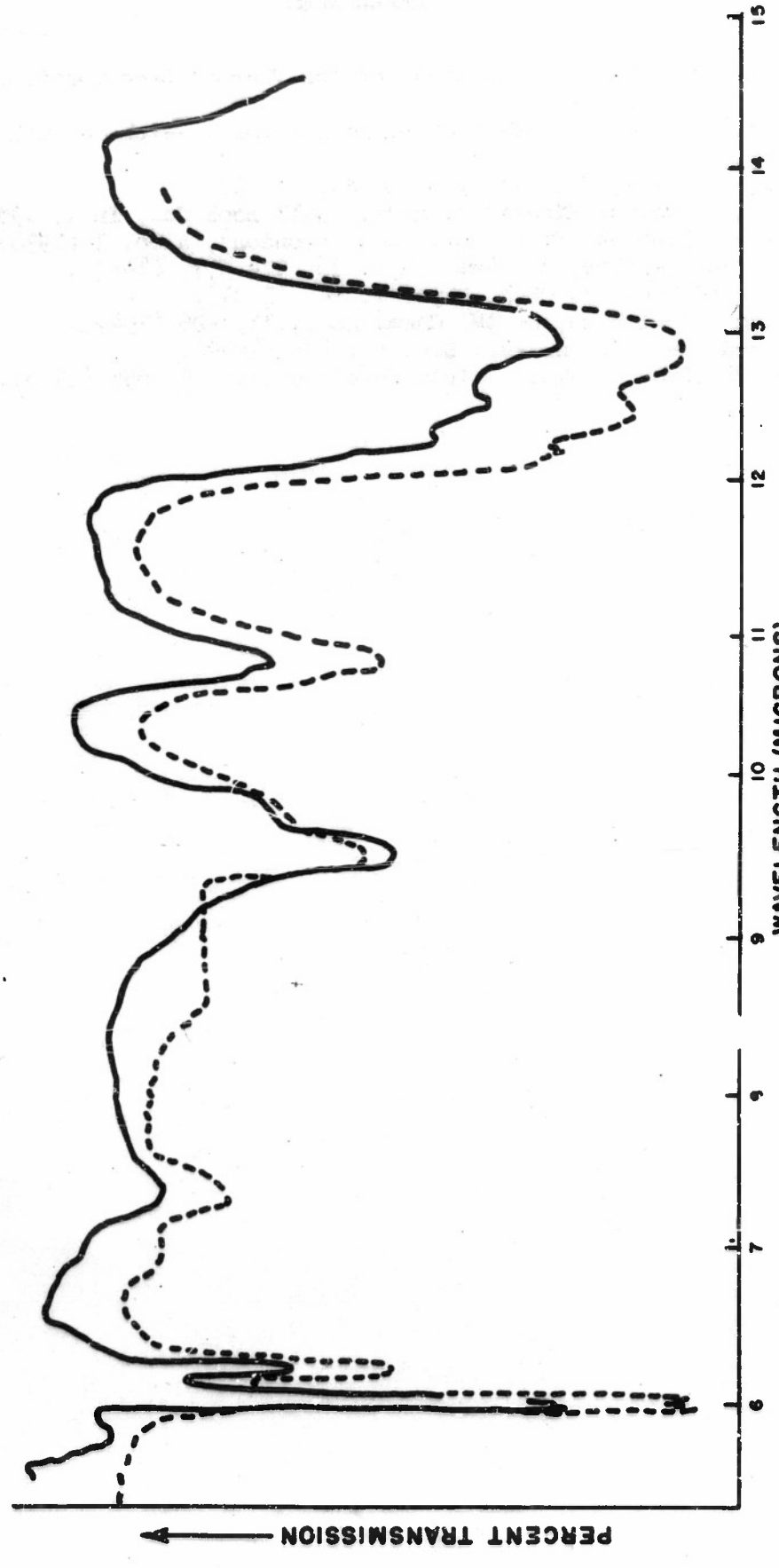

FIG. 1

SPECTRUM OF: —— PRODUCT OF $C_2H_5OOC_2H_5$-NO REACTION

---PURE C_2H_5ONO (CURVE DISPLACED DOWNWARD)